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Yoo and Boatz, "Theoretical Study of Decomposition Mechanism of High Energy Density Materials"

Poster Session **HEDM Conference**

(Statement A)

Theoretical Study of Decomposition Mechanism of High Energy Density Materials

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AFOSR HEDM CONTRACTOR'S MEETING
6/8-6/10, 1999
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Abstract

One of the HEDM research efforts has focused on the development of high performance monopropellants ~~in~~ as a replacement for hydrazine due to its toxicity. A proposed area of research involves determination of decomposition mechanisms and stabilities of monopropellants by using *ab initio* quantum mechanical calculations. Decomposition mechanisms of $[NH_2Me_2]^+[NO_3]^-$, and $[NH_2(NH_2)_2]^+[NO_3]^-$ were investigated. The potential energy surfaces of two gas-phase decomposition processes have been explored: (1) proton transfer and (2) Me^+/NH_2^+ transfer reactions. Transition states for both pathways have been located at the RHF/6-31G* level and single point energies at the MP2/6-31G*//RHF/6-31G* level have been calculated. Comparison of similarities and differences between these two systems will be presented here. Future research will involve characterization of the potential energy surface for $[NH_2NMe_2NH_2]^+[NO_3]^-$ and design of potential catalysts that will stabilize transition states.

$$[NH_2Me_2]^+[NO_3]^- \rightarrow NHMe_2 + HNO_3 \qquad (1a)$$
$$[NH_2Me_2]^+[NO_3]^- \rightarrow NH_2Me + MeNO_3 \qquad (2a)$$

$$[NH_2(NH_2)_2]^+[NO_3]^- \rightarrow NH(NH_2)_2 + HNO_3 \qquad (1b)$$
$$[NH_2(NH_2)_2]^+[NO_3]^- \rightarrow NH_2NH_2 + NH_2NO_3 \qquad (2b)$$

Background

Hydrazine is the state of the art monopropellant currently. However, it has several disadvantages including toxicity, volatility, and handling.

Researchers are continually looking for new monopropellant candidates which include energetic materials such as substituted ammonium salts.

Our research effort has concentrated on the decomposition routes of some HEDM materials. *Ab initio* quantum mechanical calculations have been carried out by our group to explore possible decomposition mechanisms.

The model compounds under study are $[NH_2Me_2]^+ [X]^-$, where $X = NO_3$ and Cl, and $[N(NH_2)_2Me_2]^+ [NO3]^-$.

Objectives:

- To map out the potential energy surface of these model compounds
- To determine the energetics of decomposing species
- To design a catalyst that stabilizes the transition state

Gaseous products detected from experimental thermal decomposition studies of $N(NH_2)_2(Me_2)NO_3$ are N_2, NH_3, H_2O and CH_4.[1]

Possible reaction pathways leading to the final products are the following:
$R, R' = H, CH_3$; $X = NO_3^-$

(1) $[N(NH_2)_2RR']^+[X]^- \rightarrow [N(NH_2)_2R'] [RX]$
(1b) $[N(NH_2)_2RR']^+[X]^- \rightarrow [N(NH_2)RR'] [NH_2X]$

(2a) $N(NH_2)_2R' \rightarrow N(NH_2)R' + NH_2$
(2b) $N(NH_2)RR' \rightarrow NRR' + NH_2$

(3) $[N(NH_2)_2RR']^+ \rightarrow RH + [NH_3R']^+ + N_2$

(4a) $NH_2X \rightarrow NH_2 + X$
(4b) $NH_2 + NH_2X \rightarrow NH_3 + NHX$
(4c) $X + NH_2X \rightarrow HX + NHX$
(4d) $2NHX \rightarrow X\text{-}NH\text{-}NH\text{-}X$
(4e) $X\text{-}NH\text{-}NH\text{-}X \rightarrow 2HX + N_2$

[1]Rubtsov, Y. I.; Andrienko, L. P.; Titova, K. V.; Loginova, E. N. *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* **1982**, *9*, 1953.

Decomposition Mechanisms of $[NH_2(NH_2)_2]^+[X]^-$, $X = Cl$ or NO_3

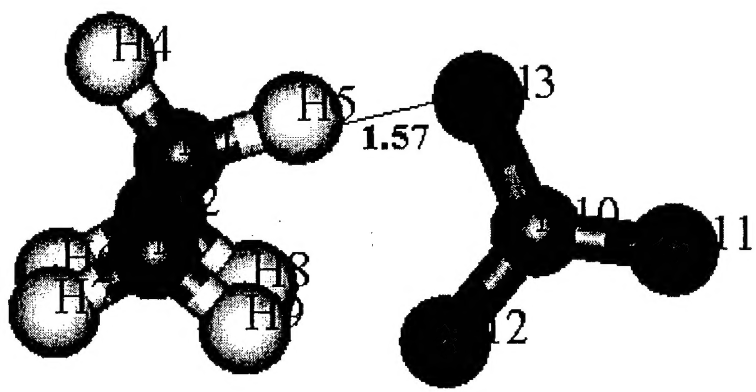
Proton Transfer

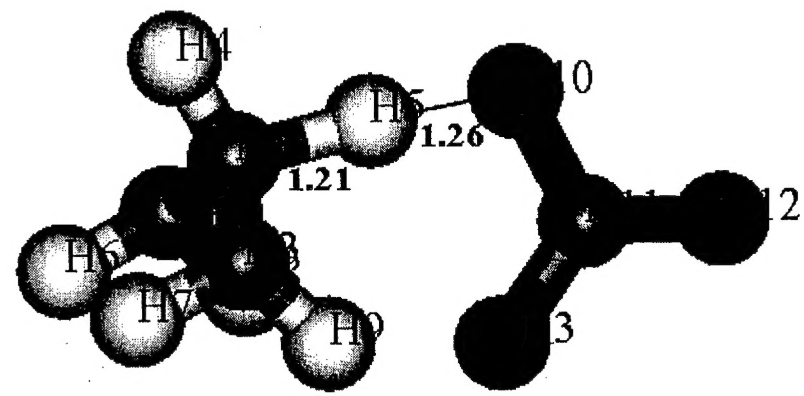
$$[NH_2(NH_2)_2]^+[X]^- \rightarrow NH(NH_2)_2 + HX$$

NH_2 Cation Transfer

$$[NH_2(NH_2)_2]^+[X]^- \rightarrow NH_2NH_2 + NH_2X$$

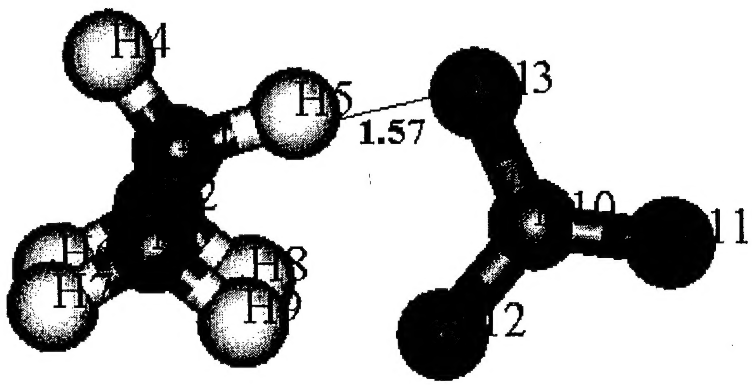
A Proton Transfer Transition Structure of $[NH_2(NH_2)_2]^+[NO_3]^-$ At RHF/6-31G*(6d)

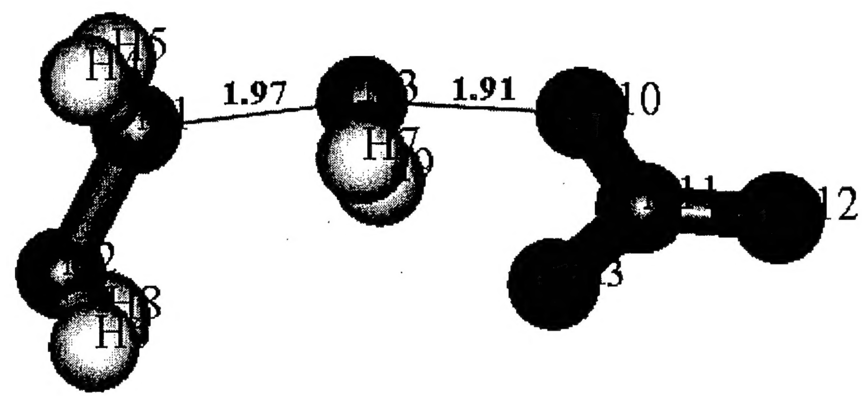




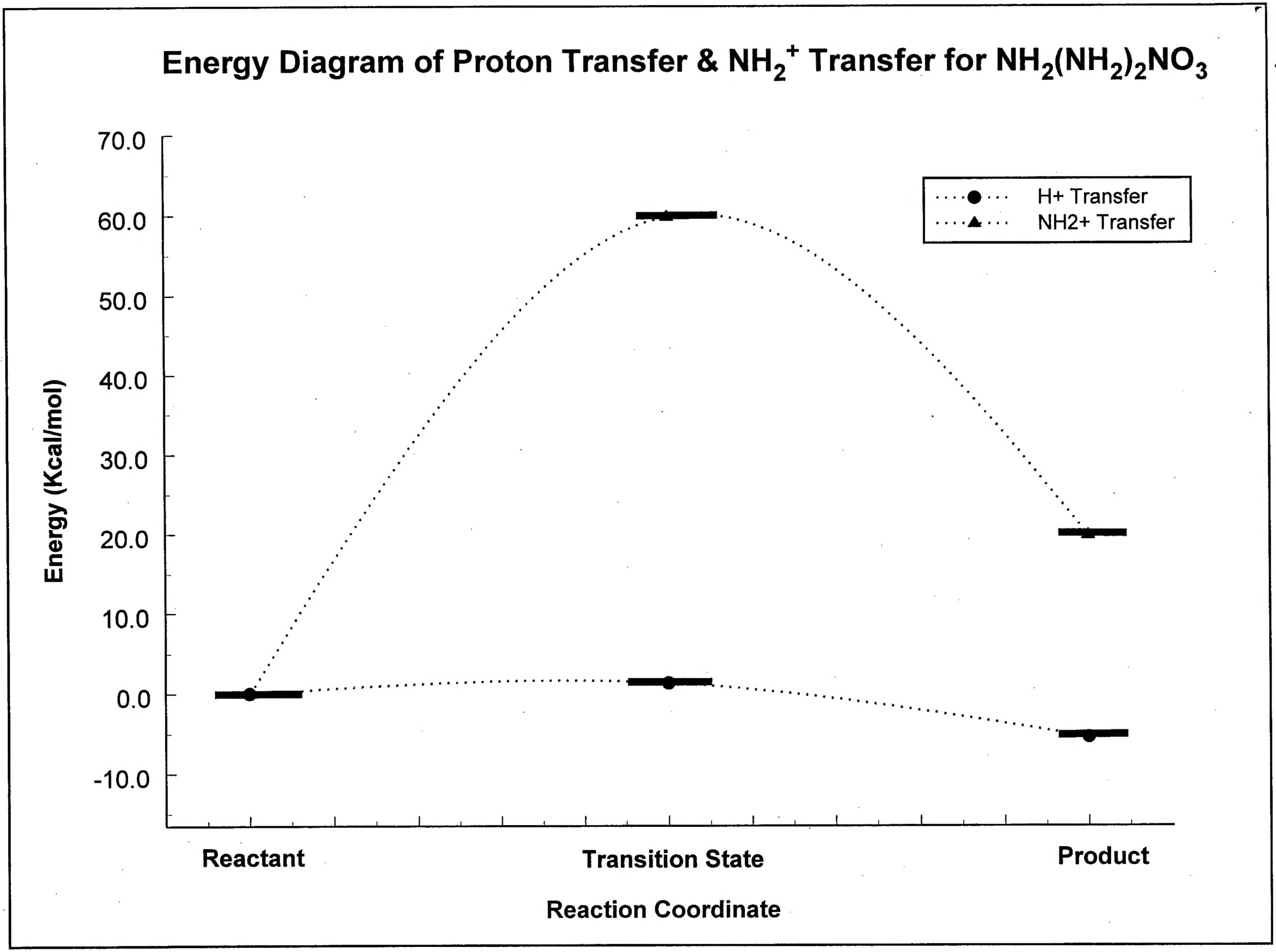
	Intermediate Complex	Transition Structure
Energy (kcal/mol)	**0.0** **(0.0)**	**1.3** **(-1.2)**

A NH_2^+ Transfer Transition Structure of $[NH_2(NH_2)_2]^+[NO_3]^-$ At RHF/6-31G*(6d)

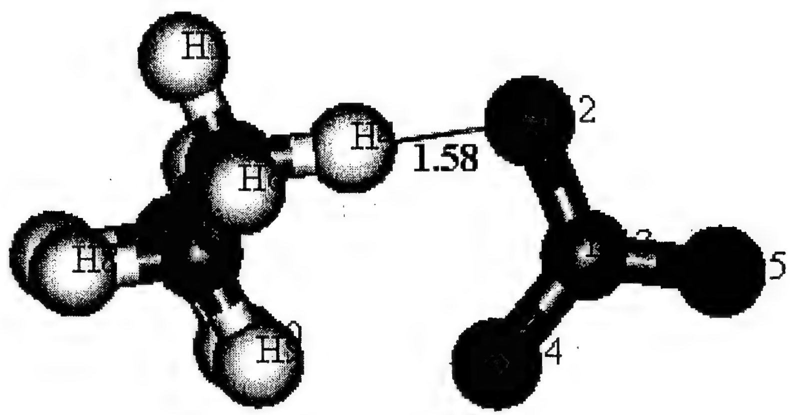


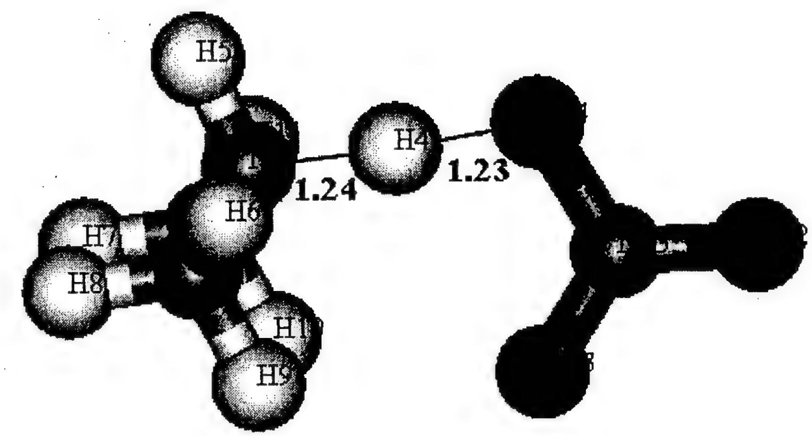


	Intermediate Complex	Transition Structure
Energy (kcal/mol)	**0.0** (0.0)	**59.8** (55.9)


Energy Diagram of Proton Transfer & NH2+ Transfer for NH2(NH2)2NO3
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
Energy (Kcal/mol)
H+ Transfer
NH2+ Transfer
Reactant
Transition State
Product
Reaction Coordinate

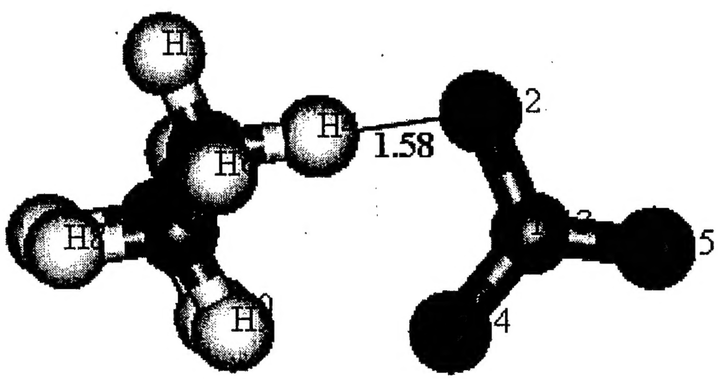
A Proton Transfer Transition Structure of $[NH_2Me_2]^+[NO_3]^-$ At RHF/6-31G*(6d)

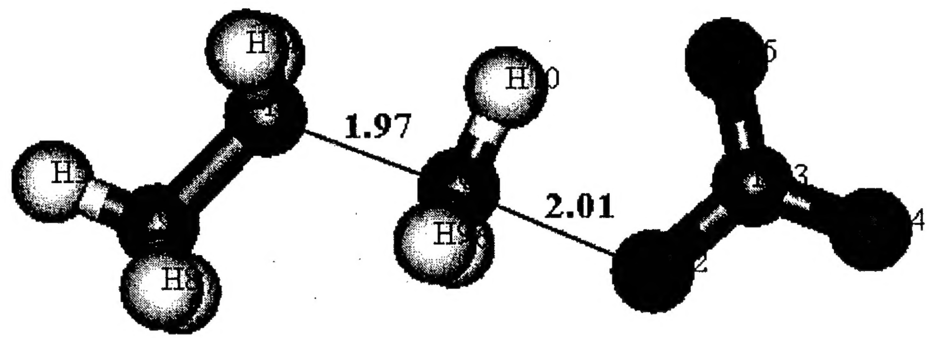




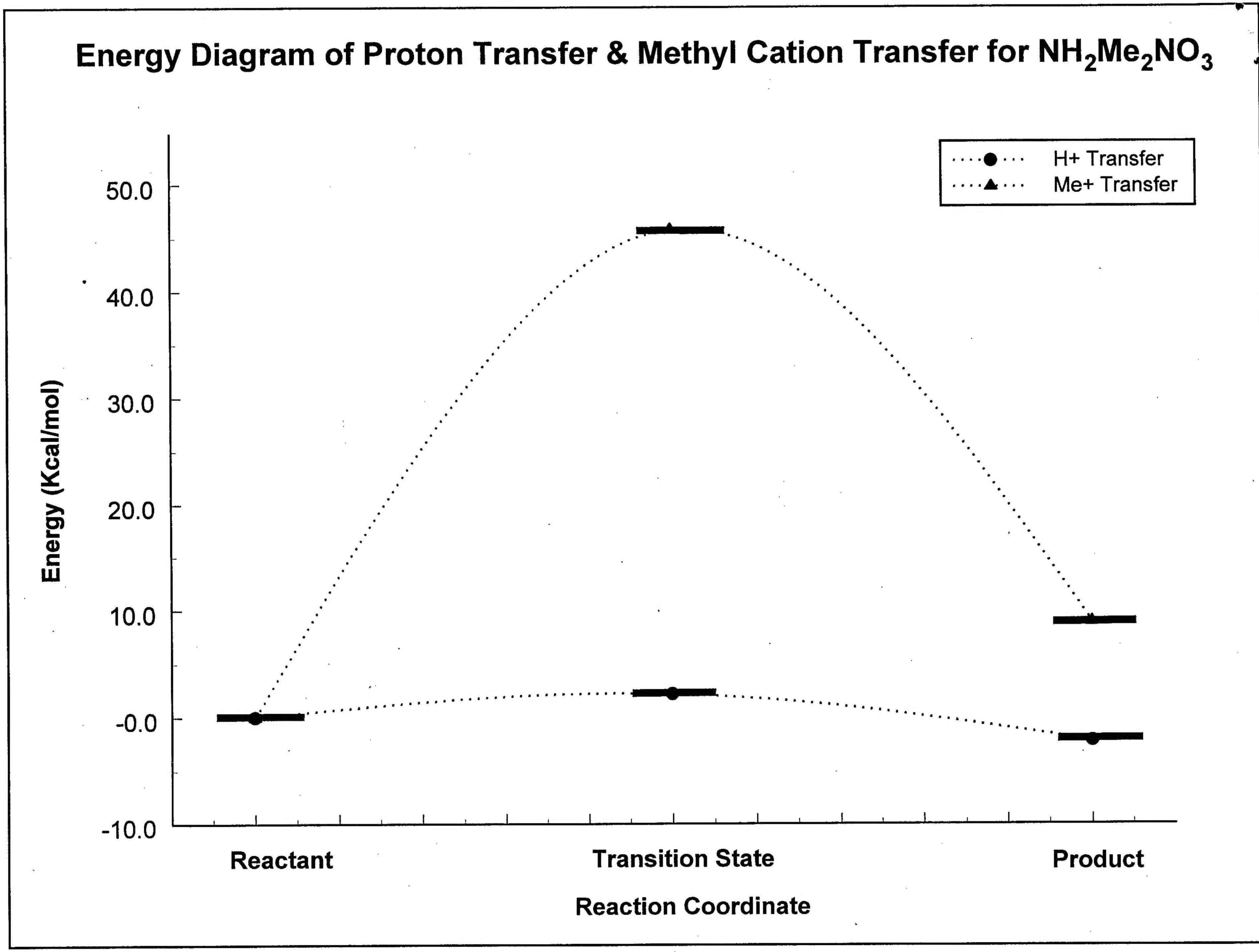
	Intermediate Complex	Transition Structure
Energy (kcal/mol)	**0.0** (0.0)	**2.2** (-1.3)

A Me^{+} Transfer Transition Structure of $[NH_2Me_2]^{+}[NO_3]^{-}$ At RHF/6-31G*(6d)





	Intermediate Complex	Transition Structure
Energy (kcal/mol)	**0.0** **(0.0)**	**45.8** **(47.7)**


Energy Diagram of Proton Transfer & Methyl Cation Transfer for $NH_2Me_2NO_3$
H+ Transfer
Me+ Transfer
Energy (Kcal/mol)
50.0
40.0
30.0
20.0
10.0
-0.0
-10.0
Reactant
Transition State
Product
Reaction Coordinate

Conclusion

Based on the *ab initio* calculation studies of $[NH_2(NH_2)_2]^+[NO_3 \text{ or } Cl]^-$ and $[NH_2(Me)_2]^+[NO_3 \text{ or } Cl]^-$

- The transition structure of proton transfer is earlier than that of methyl(or NH_2) cation transfer and also lower in barrier.

- Variations on anions or cations did not affect on the energy barrier or the transition structure.

- Since variations on cations did not affect on the energy barrier, our calculations imply that methyl cation transfer of $[NMe_2(NH_2)_2]^+[NO_3]^-$ will be favorable than NH_2^+.

Future Work

- The decomposition mechanism of $[NMe_2(NH_2)_2]^+[NO_3]^-$ as well as other ammonium salt monopropellant candidates will be investigated theoretically.

- Different catalysts will be included in the calculations for determining the potential energy surface of $[NMe_2(NH_2)_2]^+[NO_3]^-$ and it will be compared with the uncatalyzed potential energy surface.